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Novel silver-based ternary alloy

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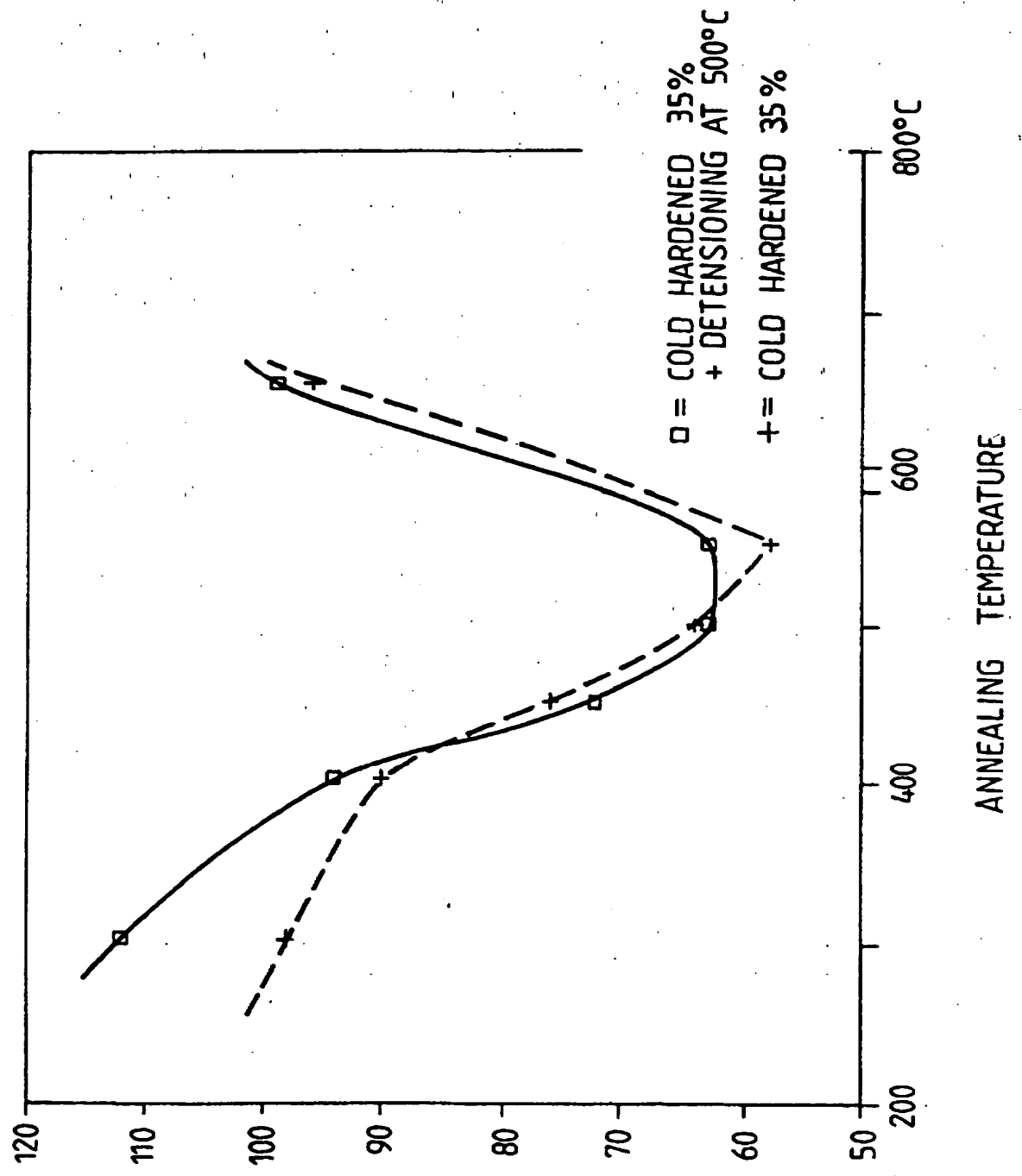
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NOVEL SILVER-BASED TERNARY ALLOY

The present invention relates to silver-based alloys.

In the fields of jewellery, gold/silver plating, coins and medals, it has been standard practice for centuries to add copper to silver. It gives the soft and ductile silver a satisfactory hardness, whilst safeguarding its original malleability and lustre.

In numerous countries, legislation defines at least two minimum silver content levels, referred to as the first and second standards. For example, minimum standards of 92.5 and 80% by weight silver are generally in force in continental Europe. The first standard silver for jewellery normally contains 92.5% silver, the remainder being copper.

However, for specific applications, such as certain worked articles, cadmium may optionally be added or entirely take the place of the copper in order to optimize the ductility/hardness ratio and increase the melting point.

A well-known disadvantage of Ag-Cu alloys is the tendency of the copper to oxidise even when alloyed with silver, and which occurs both at high and low temperatures. Therefore, in the industrial processing cadmium-free Ag-Cu alloys the oxidation of the copper leads to the following problems: In the case of castings (particularly continuous, bath or lost wax casting), the resulting oxygen inclusion in the molten bath leads to a reduction of castability, to the formation of pores on cooling and, as a consequence, the embrittlement of the cast alloy. In the case of detensioning and brazing operations, dark spots, known as "fire spots", appear in the metal during flame annealing.

Where cadmium is present in these alloys, whether as a complete or partial replacement for copper, they are difficult to handle in confined spaces because of the known toxicity of cadmium vapour. This makes it necessary to take special safety measure when handling these alloys, thus placing various constraints on the user and manufacturer of these alloys.

Finally there is the known problem of head or top contraction or shrinkage of ladle cast silver ingots, which requires the removal of a significant quantity of material from the ingot prior to further processing.

In order to overcome the problems due to the oxidation of copper in Ag/Cu alloys, it is necessary either to operate under a controlled atmosphere, or more simply to use deoxidizing fluxes to protect the surface of the alloy. Alternatively intense, repeated polishing operations can be carried out after cooling. In any event, there will be significant material and/or time losses as a result of such countermeasures.

As an alternative to copper and cadmium in silver-based precious alloys various publications in the electronic, dentistry and jewellery fields have mentioned the use of germanium. However, these mainly merely list germanium as a possible additive, due to the deoxidation properties among various other possible metalloids, but without indicating any precise content within the alloy. For example French Patent No. 922 234 suggests completely replacing the copper in an Ag-Cu alloy by one or, preferably several, other metals and, if appropriate, a metalloid. Amongst those metals germanium is referred to as a possibility, but without any specific example being given to the use of germanium. Nor is there any mention of using both copper and germanium in a silver-based alloy.

Against that a ternary Ag-Cu-Ge alloy for dental use is disclosed in US Patent 4 124 380. However that alloy contains only 40 to 85% by weight silver and would not therefore be useful in the field of first standard jewellery alloys, where the silver content by weight must be at least 92.5%.

In accordance with the present invention a novel alloy is provided which, whilst maintaining the properties inherent in Ag-Cu alloys and in particular hardness and lustre substantially eliminates the aforementioned disadvantages of such Ag-Cu alloys.

More particularly, the present invention is based on the discovery that these problems can largely be overcome using a ternary alloy of silver copper and germanium, and by means of a detailed metallurgical study of the association between silver, copper and germanium it has been possible to determine an optimum germanium content range which provides alloys fully complying with user quality requirements whilst avoiding processing difficulties and increased costs which have hitherto existed. Moreover, the retention of a small amount of copper leads to a reduced germanium content for first

standard silver alloys, and thus reduces the cost of the alloy.

The novel ternary Ag-Cu-Ge alloys of this invention are those containing a minimum of 92.5% by weight silver, 0.5 to 3% by weight germanium and the remainder apart from impurities, copper. Preferred
5 are those which contain 1.5 to 3% by weight germanium.

Despite the presence of a small but still significant amount of copper, such alloys have proved stainless in ambient air during conventional production, transformation and finishing operations.

In addition, the alloys of the present invention are easily
10 deformable cold and, in particular, are drawable, rollable or stampable, and in all such operations have a perfect mechanical
behaviour. They can also be easily brazed with appropriate addition
alloys, and do not give rise to any significant shrinkage upon casting.

The very satisfactory behaviour of the alloys according to the
15 present invention is believed to be due to the fact that germanium,
which has a greater affinity for oxygen than silver and copper, fulfils a protective function, not only in the molten alloy, but also in the ready-to-use solid alloy.

The latter property is based on the fact that in alloys
20 containing that amount of germanium, the germanium is present as a solid solution in both the silver and copper phases. Therefore the microstructure of the alloy is largely constituted by two phases, namely a germanium and copper solid solution in the silver, surrounded by a filamentous solid solution of germanium and silver in copper,
25 which itself contains a few intermetallic Cu-Ge phase dispersoids.

The presence of germanium in solid solution ensures that the
alloy does not become brittle. By contrast, silicon which, whilst being insoluble in silver and slightly soluble in copper, gives rise to alloys which are brittle to varying degrees.

30 In order to keep the germanium in solid solution, it is necessary
to limit the germanium content of the alloy to 3% by weight maximum, ||| ✓
beyond that Cu-Ge intermetallics, or pure Ge, both of which are very brittle, precipitate to a considerable extent at the grain boundaries of the argentiferous phase.

35 In addition, it is necessary to keep the germanium in solid solution in the copper-rich phase in order to inhibit surface oxidation of the copper phase, probably by the formation thereon of a very thin

GeO protective coating (or GeO_2 at temperatures above 650°C), which is transparent and invisible to the eye. It is this mechanism which prevents the appearance of dark "fire spots", e.g. during brazing and flame annealing phases, and it has been estimated that the effectiveness of this mechanism theoretically requires a minimum germanium content of germanium of approximately 0.5%. However, practical experience has shown that the above effects are optimised at germanium contents of 1.5% or above.

In the liquid state, the protective function of germanium is manifested by the formation of $(\text{GeO}/\text{GeO}_2)$ helixes "floating" on the surface of the molten bath, and to some extent forming a reducing layer on the melt.

Thus, the alloys of the present invention ensure their autoprotection with respect to oxygen throughout the production and transformation cycle. Moreover, due to the preferred sulphurization of germanium compared with silver, the alloys of the present invention tarnish or blacken much less rapidly than conventional silver-copper alloys.

Thus, the ISO 4538-1978 or "thioacetamide" test was carried out simultaneously for pure 99.99% silver, an Ag-Cu alloy with 7.5% copper, an Ag-Ge alloy with 4% germanium and an Ag-Cu-Ge alloy according to the invention with 5.5% Cu and 2% germanium.

All the samples were in the form of rectangular parallelepipeds ($1\text{cm}^2 \times 3$ to 5 mm thick), coated in an inert resin in such a way that only the 1 cm^2 face ($1\text{ }\mu\text{m}$ polished quality) is exposed to the actual corrosion test. The results are given in table I:

Alloy	Spot appearance time	Comments
Ag 99.99%	2 hours	uniform black colour
Ag+Cu 7.5%	1 hour $30 < t \leq$ hours	reddish colour on periphery and yellowish in centre
30 Ag+Cu 5.5% +Ge 2%	6 hours	pale yellow film on the periphery
Ag+Ge 4%	10 hours $< t \leq 22$ hours	black colour on periphery and yellowish in the centre

35 With regards to the mechanical properties of the Ag-Cu-Ge alloys

according to the invention, they are essentially those of a two-phase material, namely a hard phase (the copper phase) surrounding a softer phase (the silver phase), the latter being in a spatial majority and occupying approximately 85% of the space. These two phases combine to ensure at certain temperatures a hardness equal to or greater than that of a conventional Ag-Cu alloy with 7.5% Cu, together with a better tensile strength, as will be shown in the following examples.

Tests

The physical properties of two examples of alloys according to the present invention were studied in comparison with three reference alloys. These tests in particular revealed the structural hardening function of Ge within the crystal lattice of the silver, whilst keeping its ductility intact.

The following table II indicates the physical properties of the five alloys, namely the three reference alloys:

Ag-Cu with 7.5% copper (alloy No. 0)

Ag-Cu with 7.5% cadmium (alloy No. 1)

Ag-Ge with 4% germanium (alloy No. 2),

the first two being standard alloys and two first standard alloys according to the invention:

Ag-Cu-Ge with 5% Cu and 2.5% Ge (alloy No. 3)

Ag-Cu-Ge with 6% Cu and 1.5% Ge (alloy No. 4)

✓ in range
✓ in range

TABLE II

Alloy composition
Properties

Alloy 0 Alloy 1 Alloy 2 Alloy 3 Alloy 4

Melting range (°C) *

800-900 925-940 760-880 785-900 785-900

Hardness VH *
(Vickers at 150N, kg.mm⁻²)

66-75 75 40-45 70 80

Elastic limit at A=0.2%
(Re in kg.mm⁻²) *

- - 5 15-20 10-15

Tensile strength
(Rm in kg.mm⁻²) *

25-28 - 28-32 48-57 41-50

Elongation (A in %) *

40-45 - 45-50 10-20 10-20

Critical cold hardening level
(E in %)

50-55 - 25-30 30-35 35-40

Critical hardness VH at E%
(Vickers at 150N, kg. mm⁻²)

115-145 100 120 180 195

* All these figures are given for alloys annealed at 450°C and tempered in ambient air for alloys 2, 3 and 4.

In particular it is possible to see the superior ductility and tensile strength of the alloys according to the invention.

A study was also carried out on the influence of the annealing temperature (300 to 650°C) on the hardness of alloy No. 3, cold hardened at its critical level. A crude cold rolled sample was compared with a rolled sample which had been detensioned at 500°C.

The attached drawing shows the evolution of the Vickers hardness VH as a function of the annealing temperature for an annealing time (uninfluential) preferably between 2 and 4 hours. The rise in the hardness at 650°C is to a recrystallization, which modifies the previously described microstructure.

Thus, the recrystallization starting temperature is about 600 to 650°C, so that the annealing temperature must always be lower, so as to retain all the intrinsic qualities of the alloy according to the invention.

Furthermore, the increase in the hardness at low annealing temperatures typically below approximately 400°C is characteristic of a structural hardening, which is more effective when the alloy has been detensioned beforehand. This structural hardening was noted for all the ternary alloys according to the invention. For example, annealing a 200°C for 2 hours on alloy No. 4 led to a hardness rise to approximately 140 VH.

The use of conventional grain refining agents was also tested in order to displace towards the highest temperatures the recrystallization temperature range. Thus, for example, gold and nickel were added at different low contents (remaining below 0.1% for nickel). Therefore the hardness could be blocked between 60 and 65VH, even after torch annealing operations at 650°C, the addition of nickel preventing any evolution of the microstructure, even at these temperatures.

The explanation is that nickel is not miscible with silver, either in the solid state, or in the liquid state, but is miscible in any proportion with copper. It is therefore able to reduce the activity of copper with respect to germanium in the copper-rich phase, i.e. oppose the formation of Cu-Ge phase dispersoids, which then decompose at these temperatures. For similar reasons, manganese or platinum can be envisaged as substitutes for nickel.

Thus, tests carried out in connection with the influence of the annealing on the duration reveal that the latter can easily be regulated to a given value by an appropriate choice of an annealing temperature e.g. between 200 and 500°C.

5 Thus, a preferred process for producing a piece of jewellery or the like can consist of producing the crude part by casting using an Ag-Cu-Ge alloy according to the invention with a hardness of e.g. 70 to 80 VH, working the part (engraving, etc.), which is then relatively malleable and then carrying out annealing (20 minutes to 2 hours, as a
10 function of the weight of the part) at an appropriate temperature to obtain the requisite final hardness.

As indicated, the invention is primarily directed to silver alloys capable of meeting the first standard for silver-containing jewellery alloys that is to say containing at least 92.5% silver.
15 Amounts of silver may be as high as 96% with a corresponding reduction in the copper component of the alloy. Thus over all, the range of ternary alloys covered by this invention are those containing, apart from impurities, 92.5 to 96% silver, 0.5 to 3.0% germanium, preferably 1.5 to 3%, and 1 to 7% copper. Preferred are those containing, apart
20 from impurities, 92.5% silver, 0.5 to 3.0% germanium and 1 to 7% copper, and especially those containing 92.5% silver, 1.5 to 3.0% germanium and 4.5 to ⁶7% copper.

CLAIMS

1. A ternary alloy of silver, copper and germanium containing on a weight basis 92.5% silver minimum, 0.5 to 3% germanium and the remainder, apart from impurities, copper.
5
 2. An alloy according to claim 1, containing on a weight basis, and apart from impurities, 92.5 to 96% silver, 0.5 to 3% germanium, 1 to 7% copper.
10
 3. An alloy according to claim 1 or 2, which contains from 1.5 to 3% by weight germanium.
 4. An alloy according to claim 1, containing on a weight basis, and apart from impurities, 92.5% silver, 0.5 to 3% germanium and 4.5 to 7% copper.
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 5. An alloy according to claim 1, containing on a weight basis, and apart from impurities, 92.5% silver, 1.5 to 3% germanium and 4.5 to 6% copper.
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 6. A method for the production of silver or silver plated jewellery, coins or medals, or other articles wherein there is used an alloy as claimed in any one of claims 1 to 5.
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 7. An article of manufacture comprising or consisting of an alloy according to any one of claims 1 to 5.
 8. An article of manufacture according to claim 7, which is an item of jewellery, a coin or a medal.
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